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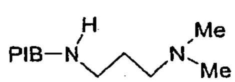
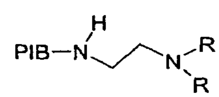
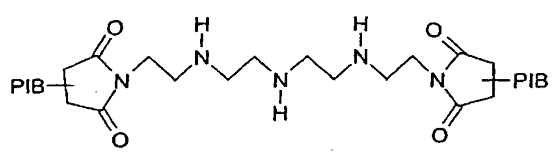


PIBamines

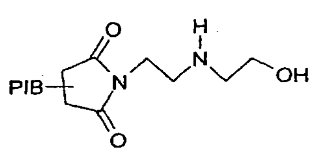


(R=H or Me)

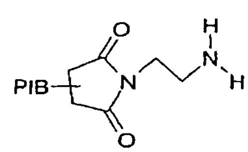
1000/EDA,DMAPA



1000/b/TEPA PIBSI



1000/m/AEEA PIBSI



1000/m/EDA PIBSI

(57) **Abstract:** The present invention provides a composition comprising (i) an aviation fuel; and (ii) a deposit inhibiting compound of the formula P-Q-R in which P is a polymeric hydrocarbyl group in which Q is an optional ring system ; in which R is a group selected from H and hydrocarbyl; wherein if R is a hydrocarbyl group it is free of a carboxylic acid group (-COOH); wherein Q together with R contains no greater than 2 nitrogens; and wherein when Q together with R contains 2 nitrogens each of the nitrogens is a member of a heterocyclic ring.

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COMPOSITION

The present invention relates to a composition comprising an aviation fuel and a deposit inhibiting compound.

As discussed in US-A-5621154, turbine combustion fuel oils i.e. jet fuels, such as JP-4, JP-5, JP-7, JP-8, Jet A, Jet A-1 and Jet B are ordinarily middle boiling distillates, such as kerosene or combinations of naphtha and kerosene. Military grade JP-4, for instance, is used in military aircraft and is a blend of naphtha and kerosene. Military grades JP-7 and JP-8 are primarily highly refined kerosenes, as are Jet A and Jet A-1, which are used for commercial aircraft. Civil grades of jet fuel are defined in ASTM D1655, DefStan 91-91, and other similar specifications. Such jet fuel are produced from a variety of sources including crude oil, oil sands, oil shales, Fischer Tropsch processes and gas to liquid processes. Refinery processing includes fuels produced by straight distillation, sometimes processed by chemical sweetening, or hydrogen processing including hydrocracking operations, and may contain <1 to 3000 ppm sulphur.

Turbine combustion fuel oils often contain additives such as antioxidants, metal deactivators, corrosion inhibitors and lubricity improvers. These additives are often necessary in these fuel oils to meet defined performance and storage requirements.

Turbine combustion fuel oils are used in integrated aircraft thermal management systems to cool aircraft subsystems and the engine lubricating oil. The turbine combustion fuel oil is circulated in the airframe to match heat loads with available heat sink. In current aircraft, these thermal stresses raise bulk fuel temperatures to as high as 425°F at the inlet to the mainburner fuel nozzles and above 500°F inside the fuel nozzle passages. In the augmentor or afterburner systems, skin temperatures up to 1100°F are experienced. In future aircraft, these temperatures are expected to be 100°F higher.

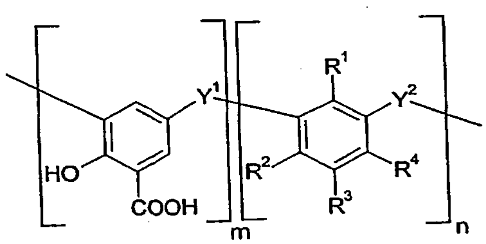
At these high temperatures (425°F-1100°F) and oxygen-rich atmospheres in aircraft and engine fuel system components, fuel degrades forming gums, varnishes, and coke deposits. These deposits plug-up the components leading to operational problems including reduced thrust and performance anomalies in the augmentor, poor spray patterns and premature failure of mainburner combustors and problems with fuel

controls. Further, the engine exhaust becomes smoky and sooty and engine noise increases, both of which are undesirable characteristics for jet engines.

The problems of deposition from fuels at elevated temperatures is not limited to the use of fuels in the extreme environments encountered in aviation. As discussed in WO-A-99/25793 in some oil fired devices, such as boilers and slow heating cookers, e.g. of the Aga type, kerosene oil fuel is passed down a narrow metal feed pipe to the combustion chamber where it is burnt. Parts of the pipe are sufficiently near the hot chamber for them to be heated to significant temperatures, resulting in the risk of thermal degradation of the fuel in the pipe, especially with slow feed rates and high residence times in the pipe. This degradation can form solid deposits which reduce the flow and ultimately stop it, causing the combustion to stop. To overcome this manufacturers of such devices have for many years recommended to their users that at least once each six months such pipe parts are cleaned of solid deposits of coke or other materials.

Detergent additives for inhibiting the oxidation of fuels and the inhibition of deposit formation in engines have been proposed.

WO-A-99/25793 discloses compounds which are taught to be thermal stabilising additives for fuels comprising kerosene and jet fuels. The compounds are oil soluble macromolecules and comprise a hydroxy-carboxylic acid functionality. Typically compounds of WO-A-99/25793 are of the formula



wherein Y^1 and Y^2 are divalent bridging groups, which may be the same or different; R^3 is hydrogen, a hydrocarbyl or a hetero-substituted hydrocarbyl group ; each of R^1, R^2 and R^4, which may be the same or different, is hydroxyl hydrogen, hydrocarbyl or hetero-substituted hydrocarbyl, with the proviso that at least one of R^1, R^2, R^4 is hydroxyl, and m+n is 4 to 20, m is 1-8 and n is at least 3.

US-A-5621154 similarly relates to methods for cleaning and inhibiting deposit formation on jet engine surfaces such as fuel intake and combustion components during the

combustion of turbine combustion fuel oils. There is disclosed the addition to the turbine combustion fuel oil prior to its combustion a derivative of a polyalkenylthiophosphonic acid (PATPA). The derivatives of polyalkenylthiophosphonic acid are prepared in accordance with US-A-3281359. Compounds in accordance with the teaching of US-A-5621154 have found some success and have been used by the United States Air Force (USAF) for the purposes disclosed.

An important factor in determining the suitability of additives for jet fuel is affinity of the additives for water. One skilled in the art readily appreciates that the inclusion of water in a jet fuel is problematic. For this reason fuels, in particular aviation fuels, are often passed through a coalescer prior to fueling. The coalescer removes water which may cause problems if it enters the combustion chamber of an engine or it freezes in an aircraft fuel system, typically in the fuel tanks, at high altitude, preventing delivery of fuel to the engine. This may be result in failure of the engine. These problems are particularly noted in systems in which fuel may be stored in a tank which also contains water. Some such systems are used on naval vessels where, to maintain the ballast of a vessel, as fuel is removed from storage tanks it is replaced with water. However, fuel additives such as detergents can de-activate the media in coalescers, reducing their ability to coalesce and remove entrained water from fuels.

The compounds of US-A-5621154 have been found to inhibit separation of water from fuels passed through a coalescer. For this reason, the USAF require that the additives of US-A-5621154 be combined with fuel at the skin of the aircraft. Mixing of the fuel and additive prior to fuelling of the aircraft is prohibited.

The present invention alleviates the problems of the prior art.

Aspects of the invention are defined in the appended claims.

In one aspect the present invention provides a composition comprising (i) an aviation fuel; and (ii) a deposit inhibiting compound of the formula I

$$\text{P-Q-R (I)}$$

in which P is a polymeric hydrocarbyl group; in which Q is an optional ring system; in which R is a group selected from H and hydrocarbyl; wherein if R is a hydrocarbyl group it is free of a carboxylic acid group (-COOH); wherein Q together with R contains no

greater than 2 nitrogens; and wherein when Q together with R contains 2 nitrogens each of the nitrogens is a member of a heterocyclic ring.

In one aspect the present invention provides use of a deposit inhibiting compound as defined herein for

(i) the inhibition of deposit formation in a composition comprising the compound and a fuel, preferably an aviation fuel; and/or

(ii) the inhibition of particle formation from the oxidation product(s) of a fuel, preferably an aviation fuel; and/or

(iii) the solubilisation of deposits and/or deposit precursors

In one aspect the present invention provides a method for inhibiting deposition formation in a fuel, preferably an aviation fuel, at an elevated temperature, the method comprising combining with the fuel a deposit inhibiting compound of the formula I

P-Q-R (I)

in which P is a polymeric hydrocarbyl group; in which Q is an optional ring system; in which R is a group selected from H and hydrocarbyl; wherein if R is a hydrocarbyl group it is free of a carboxylic acid group (-COOH); wherein Q together with R contains no greater than 2 nitrogens; and wherein when Q together with R contains 2 nitrogens each of the nitrogens is a member of a heterocyclic ring.

We have found that the compounds of the present invention, such as 1000/m/ButA PIBSI, act in aviation fuels to inhibit deposition of material from aviation fuels at elevated temperatures which, when present, may block filters and reduce the efficiency of an engine in which the fuel is combusted. We have found that the present compounds, which contain a limited number of nitrogens, do not de-activate the coalescing media in coalescers to the extent of compounds of, for example, US-A-5621154 when present in a aviation fuel. Thus the present compounds provide effective compounds and compositions which do not require special handling, for use in aviation fuels in which water absorption is to be avoided, such as in jet fuels. The tendency of detergents to deactivate a coalescer is commonly measured using the Micro Separometer rating (MSEP) test procedure.

The compounds of the present invention are the formula P-Q-R. R is a selected from H and hydrocarbyl with the proviso that if R is a hydrocarbyl group it is free of a carboxylic

acid group (-COOH). Q together with R contains no greater than 2 nitrogens. Furthermore, when Q together with R contains 2 nitrogens each of the nitrogens is a member of a heterocyclic ring. We have found that by the provision of such compounds a deposit inhibitory effect may be observed, for example by study using Isothermal Corrosion Oxidation Test (ICOT) or Hot Liquid Process Simulator (HLPS), without the prior art problems of de-activation of coalescing media, which may be studied by MSEP.

Without being bound by theory it is believed that the compounds of the invention are useful because limiting the number of basic nitrogens limits the polarity of the compounds. The compounds thereby retain deposit inhibitory properties whilst have a reduced tendency (either alone or together with other co-additives such as corrosion inhibitors and lubricity improvers) to be absorbed onto the surface of coalescing media, for example fibreglass, in a coalescer. The deposit inhibitory properties of the present compounds of the invention are particularly surprising as the art has previously taught that reduction of the number of nitrogens in a detergent reduces the detergency of that compound.

PREFERRED ASPECTS

In a preferred aspect Q together with R contains no greater than 1 nitrogen.

Group R

R is a group selected from H and hydrocarbyl; wherein if R is a hydrocarbyl group it is free of a carboxylic acid group (-COOH).

In the present specification by the term "hydrocarbyl group" it is meant a group comprising at least C and H and may optionally comprise one or more other suitable substituents. Examples of such substituents may include halo-, alkoxy-, nitro-, a hydrocarbon group, an N-acyl group, a cyclic group etc. In addition to the possibility of the substituents being a cyclic group, a combination of substituents may form a cyclic group. If the hydrocarbyl group comprises more than one C then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked *via* a suitable element or group. Thus, the hydrocarbyl group may contain hetero atoms. Suitable

hetero atoms will be apparent to those skilled in the art and include, for instance, sulphur, nitrogen and oxygen.

In one preferred embodiment of the present invention, the hydrocarbyl group is a hydrocarbon group.

Here the term "hydrocarbon" means any one of an alkyl group, an alkenyl group, an alkynyl group, an acyl group, which groups may be linear, branched or cyclic, or an aryl group. The term hydrocarbon also includes those groups but wherein they have been optionally substituted. If the hydrocarbon is a branched structure having substituent(s) thereon, then the substitution may be on either the hydrocarbon backbone or on the branch; alternatively the substitutions may be on the hydrocarbon backbone and on the branch.

Preferably the hydrocarbon group contains from 1 to 10, preferably from 2 to 8, preferably 2 to 6, for example 2, 4 or 6 carbon atoms. Preferably in this aspect the hydrocarbon group is a straight chain.

In a preferred aspect R is a nitrogenous hydrocarbyl group.

The term "nitrogenous hydrocarbyl group" as used herein means a group comprising at least C, H and N and may optionally comprise one or more other suitable substituents. Examples of such substituents may include halo-, alkoxy-, an alkyl group, a cyclic group etc. In addition to the possibility of the substituents being a cyclic group, a combination of substituents may form a cyclic group. If the nitrogenous hydrocarbyl group comprises more than one C then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked *via* a suitable element or group. Thus, the nitrogenous hydrocarbyl group may contain hetero atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for instance, sulphur.

In one preferred embodiment of the present invention, the nitrogenous hydrocarbyl group is a nitrogenous hydrocarbon group.

Here the term "nitrogenous hydrocarbon group" means a group containing only C, H and N (with the proviso of course that Q together with R contains no greater than 2 nitrogen)

including primary, secondary and tertiary amines, which group may be linear, branched or cyclic. The term nitrogenous hydrocarbon group also includes groups which have been optionally substituted. If the nitrogenous hydrocarbon group is a branched structure having substituent(s) thereon, then the substitution may be on either the hydrocarbon backbone or on the branch; alternatively the substitutions may be on the hydrocarbon backbone and on the branch.

Preferably the combined total of nitrogen and carbon atoms in the nitrogenous hydrocarbon group is from 1 to 10, preferably from 2 to 8, preferably 2 to 6, for example 2, 4 or 6. Preferably in this aspect the nitrogenous hydrocarbon group is a straight chain.

In a preferred aspect if R is a hydrocarbyl group it is free of a hydroxyl group (-OH).

Group Q

Q is an optional ring system. In one aspect the optional ring system Q is present.

In one aspect Q is substituted. Preferably Q is substituted with one or more groups selected from =O and –OH.

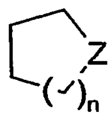
In one aspect Q is an aromatic ring.

In one aspect Q has from 4 to 10 members, preferably from 4 to 6 members, preferably 5 or 6 members.

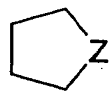
Q may be heterocyclic ring or may contain only carbon. The ring may be a hydrocarbyl ring. In the present specification by the term “hydrocarbyl ring” it is meant a cyclic group comprising at least C and H and may optionally comprise one or more other suitable ring members. Suitable ring members will be apparent to those skilled in the art and include, for instance, sulphur, and nitrogen.

In one aspect Q is a carbon ring or a heterocyclic ring containing only carbon and one nitrogen.

In one aspect Q is selected from a ring system of the formula



wherein Z is C or N and n is an integer from 1 to 5. In this aspect preferably Q is selected from a ring system of the formula



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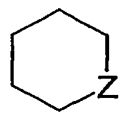
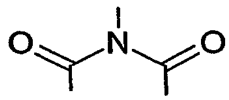
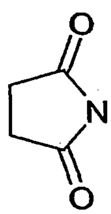


wherein Z is C or N, i.e. n is 1 or 2.

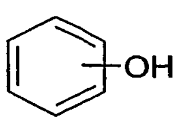
In one aspect Q contains an imide group, namely a group of the formula



Preferably Q is a ring system of the formula



In one aspect Q is a hydrocarbon ring substituted with at least one alcohol group. The hydrocarbon ring may be aromatic and in a preferred aspect is a six membered aromatic ring. Preferably Q is a ring system of the formula



In one aspect Q together with R is a Mannich group or is derived from or derivable from a Mannich reaction.

When the ring Q contains a nitrogen, preferably group R is attached to ring Q *via* the nitrogen. In other words, the nitrogen of group Q may be substituted by group R.

Group P

P may be a C_{10}-C_{200} hydrocarbyl group, preferably a C_{10}-C_{200} hydrocarbon group. P is preferably a C_{30}-C_{80} group.

In one aspect P is a branched or straight chain alkyl group. In one aspect P is a branched alkyl group.

In one aspect P is a polyalkenyl group. Preferably the polyalkenyl is a C_2 to C_6 alkenyl group, more preferably a C_4 alkenyl group.

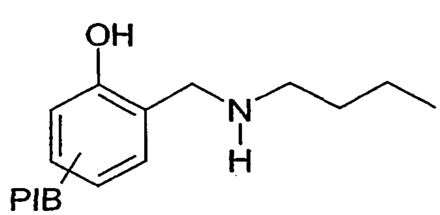
In one aspect P is polyisobutene (PIB). Conventional PIBs and so-called "high-reactivity" PIBs (see for example EP 0565285) are suitable for use in the invention. High reactivity in this context is defined as a PIB wherein at least 50%, preferably 70% or more, of the terminal olefinic double bonds are of the vinylidene type, for example the GLISSOPAL compounds available from BASF.

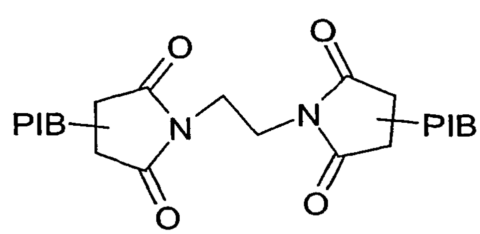
In one aspect P has a molecular weight of 200 to 2500, for example approximately 2300, including from 1000 to 2500, from 1500 to 2500, from 2000 to 2500, from 200 to 2000, and from 700 to 1300.

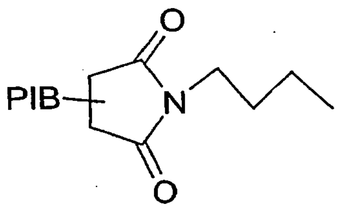
In one aspect P is polyisobutene having a molecular weight of from 1000 to 2500, from 1500 to 2500, or from 2000 to 2500.

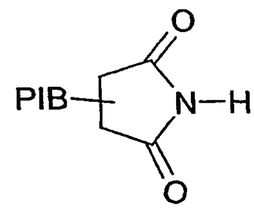
Deposit inhibiting compound

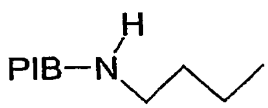
In one aspect the deposit inhibiting compound is selected from compounds of the formulae











wherein PIB is polyisobutene. Preferably PIB is polyisobutene having a molecular weight of from 1000 to 2500, from 1500 to 2500, or from 2000 to 2500.

<u>Composition</u>

The deposit inhibiting compound may be present in the composition in amount of at least 1ppm or at least 5ppm, such as 1 to 1000, 5 to 1000 for example 5 to 500, 5 to 200 or 10 to 100ppm based on the weight of the composition e.g. the fuel composition. The additive may be mixed with the jet or other fuel composition in the form of a concentrate in solution, e.g. in an aliphatic aromatic hydrocarbon in 20-80% w/w solution, or it may be added as such to give a solution in the fuel.

The composition can comprise jet fuel. The composition can comprise kerosene, in particular in jet fuel. The main component of the jet fuel itself is usually a middle boiling distillate boiling point in the range 150-300°C at atmospheric pressure and the fuel is usually kerosene which may be mixed with gasoline (naphtha) and optionally light petroleum distillate as in mixtures of gasoline and kerosene. The jet fuel may comprise mixtures of gasoline and light petroleum distillate, e.g. in weight amounts of 20-80:80-20 such as 50-75:50-25 which weight amounts may also be used for mixtures of gasoline and kerosene. The jet fuels for military use are designated JP-4 to 8 e.g. JP-4 as 65% gasoline/35% light petroleum distillate (according to US Mil. Spec. (MIL 5624G)), JP-5, similar to JP-4 but of higher flash point, JP-7, a high flash point special kerosene for advanced supersonic aircraft and JP-8, a kerosene similar to Jet AI (according to MIL 83133C). Jet fuel for civilian use is usually a kerosene type fuel and designated Jet A or Jet AI. The jet fuel may have a boiling point of 66-343°C or 66-316°C (150-650°F e.g. 150-600°F), initial boiling point of 149-221°C, e.g. 204 C (300-430°F, e.g. 400°F), a 50% boiling point of 221-316°C (430-600°F) and a 90% boiling point of 260-343°C (500-650°F) and API Gravity of 30-40. Jet fuel for turbojet use may boil at 93-260°C (200-

500°F) (ASTM D1655-006). Further details on aviation fuels may be obtained from "Handbook of Aviation Fuel Properties", Co-ordinating Research Council Inc., CRC Report No. 530 (Society of Automotive Engineers Inc., Warrendale, PA, USA, 1983) and on US military fuels, from "Military Specification for Aviation Turbine Fuels", MIL-T-5624P.

The jet fuel may be the straight run kerosene optionally with added gasoline (naphtha), but frequently has been purified to reduce its content of components contributing to or encouraging formation of coloured products and/or precipitates.

Among such components are aromatics, olefins, mercaptans, phenols and various nitrogen compounds. Thus the fuels may be purified to reduce their mercaptan content e.g. Merox fuels and copper sweetened fuels or to reduce their sulphur content e.g. hydrogen treated fuels or Merifined fuels. Merox fuels are made by oxidation of the mercaptans and have a low mercaptan S content (e.g. less than 0.005% wt S) such as 0.0001-0.005% but a higher disulphide S content (e.g. at most 0.4% or at most 0.3% wt S such as 0.05-0.25 e.g. 0.1-2%); their aromatic (e.g. phenolics) and olefins content are hardly changed. Hydrogen processed jet fuels are ones in which the original fuel has been hydrogenated to remove at least some of sulphur compounds e.g. thiols and under severe conditions to saturate the aromatics and olefins; hydrofined jet fuels have very low sulphur contents (e.g. less than 0.01% S by weight). Merifined fuels are fuels that have been extracted with an organic extractant to reduce or remove their contents of sulphur compounds and/or phenols. The jet fuel may also contain metals, either following contact with metal pipes or carried over from the crude oil, oil sands, shale oil or other sources; examples of such metals are copper, nickel, iron and chromium usually in amounts of less than 1 ppm e.g. each in 10-150 ppb amounts. Merox, straight run and hydrofined fuels are preferred and may be used in JP- 4-8 jet fuels.

The fuel comprising kerosene may also be a fuel for combustion especially for non motive purposes, e.g. power generation, steam generation, and heating, especially for use in buildings and for cooking, e.g. as described above. The fuel is particularly suitable for the devices e.g. boilers and slow cookers as described above in which there is localised preheating of the fuel before it is combusted.

Such fuels are known as burning kerosene and may have the same physical properties

as the kerosene based jet fuels described above, e.g. straight run kerosene, or kerosene modified to reduce its content of at least one of aromatics, olefins and sulphur compounds, as described above. The fuel may also contain metals as described above.

The fuel compositions of the invention contains the deposit inhibiting compound and may also contain at least one conventional additive e.g. for jet fuels or burning fuels such as an antioxidant, corrosion inhibitor, lubricity improvers, metal deactivators (MDA), leak detection additives, "special purpose" additives such as drag reducing agents, anti-icing additives and static dissipators such as Stadis®, especially in amounts each of 1-2000ppm. The deposit inhibiting compounds may be present in the composition especially with a dispersant; the dispersant is in particular one known for use in fuels e.g. automotive burning or aviation fuels. Such dispersants usually have a polymeric carbon backbone with pendant groups containing nitrogen, which may be primary, secondary or tertiary, in cyclic or acyclic systems, and especially in amine, amide or imide groupings, in particular cyclic imide groups. The dispersants may also contain 1-5 polymer chains which are bridged by the nitrogen containing groups. Examples of such dispersants are the reaction products of polyisobutene succinic anhydride (PIBSA) and polyamines. Such dispersants are known compounds for dispersing particles in non aqueous systems e.g. hydrocarbon systems. The weight ratio of deposit inhibiting compound to dispersant may be 99:1 to 10:90, especially 30:70 to 70:30. The additives and the fuel composition are preferably substantially ashless.

The use or method of the present invention is typically performed when the fuel or fuel composition is at a temperature of no greater than 1100°F. The fuel or fuel composition is typically at a temperature of 325 to 425°F during use. In a one aspect the use or method of the present invention is preferably performed when the fuel or fuel composition is at a temperature of from 100 to 335°C.

We have also found that the present invention may be applicable to a broad range of fuels, not only aviation fuels. Thus in a broad aspect the present invention provides a composition comprising (i) a fuel; and (ii) a deposit inhibiting compound of the formula I P-Q-R (I), in which P is a polymeric hydrocarbyl group, in which Q is an optional ring system; in which R is a group selected from H and hydrocarbyl; wherein if R is a hydrocarbyl group it is free of a carboxylic acid group (-COOH); wherein Q together with

R contains no greater than 2 nitrogens; and wherein when Q together with R contains 2 nitrogens each of the nitrogens is a member of a heterocyclic ring.

The present invention will now be described in further detail by way of example only with reference to the accompanying figures in which:-

Figure 1 shows compounds not in accordance with the present invention; and
Figure 2 shows compounds in accordance with the present invention.
Figure 3 shows ICOT apparatus.
Figure 4 shows HLPS apparatus.

The present invention will now be described in further detail in the following examples.

EXAMPLES

The additives shown in Figures 1 and 2 were tested for ICOT, limited HLPS and MSEP data. The Protocols for these tests are given below.

PROTOCOL I - ICOT

Scope - The ICOT is used to investigate the effectiveness of additives in jet fuel. This is carried out by stressing base and additized fuels at constant temperature with a controlled volume of air flowing though the sample. On cooling the fuels are filtered, the thermal stability measured by the weight of solid on a filter.

Summary - The ICOT is run under the following conditions, 100 ml of fuel is stressed at 180 °C with an air flow of 1.3 litres/hour for 5 hours. The fuel sample is then left to cool for 16 hours. The cooled fuel is then filtered using a 0.7 to 1μm glass microfibre filter. The weight of solid on the filter is a measurement of the fuels thermal stability under stress. By comparing base fuels to additized fuels the effectiveness of different additives can be compared.

Apparatus - See ASTM Method D4871-88 for description of apparatus. The filter to be used is a 0.7 to 1μm glass micro-fibre filter. For cleaning of glassware a furnace anneals

the glass inlet tubes and the test cell at 600 °C. Filtration is done under suction using an appropriate funnel.

Materials

Base fuels – fuels not containing additives

Additized fuels - base fuels that have been treated with additive package containing

- 100mg/l of detergent/dispersant (active ingredient);
- 25 mg/l BHT (2,6-di-t-butyl-4-methyl phenol); and
- 2mg/l of N,N'-disalicylidene-1,2-propanediamine, a metal deactivator.

Preparation - Clean glassware must be used for each experiment. The cleaning of the glass inlet tubes and the test cells is done by annealing in a furnace at 600°C then allowing cooling in air. The condensers are washed out with acetone with a small brush and wiped to ensure that no fuel residues are present, then allowed to dry in air.

Test Procedure

1. Turn heating block on and allow to heat up to a constant temperature of 180°C.
2. Number test cells and place in corresponding sites.
3. Inlet tubes and condensers are set up as shown in figure 3
4. Sites 1-5 are used for test fuel samples. Place 100 mls of test fuel in each cell by carefully releasing the condenser and inserting a glass funnel.
5. Repeat for site 6 using a control fuel.
6. Set the flows for each site to 1.3 lt/hour by adjusting the glass bead floats. (Refer to calibration chart for correct setting.
7. Reflux the fuels for 5 hours at 180°C.
8. After the 5 hours remove the inlet tubes and condensers.
9. Remove the test cells and place in a suitable stand.
10. Allow to cool for 16 hours (overnight).
11. Place all used glassware in furnace for cleaning.
12. For each sample pre-weigh a 0.7-1μm glass micro-fibre filter. Place the test cells in a ultrasonic bath for 3 minutes to release any deposit adhered to the sides of the cell, then filter the fuel under vacuum. Rinse the test cell rinsed with heptane or 2-2-4 trimethylpentane and also filter..
13. Place the filters on petri dishes and dry in a oven at 60°C for 3 hours
14. Re-weigh the filter papers and perform the calculation below.

Calculation - The information is required in mg per litre.

$$\frac{(\text{weight of filter with deposits in g}) - (\text{weight of filter in g}) \times 1000}{0.1 \text{ litre}}$$

PROTOCOL II - HLPS

Scope - HLPS is a self-contained testing apparatus designed to test the thermal properties of base and additised jet fuels. The test involves the flow of the test fuel over a heated test surface (@ 335°C) under high pressure (500psi).

Summary - The HLPS is run in accordance with ASTM D-3241. The conditions for testing are set to those used by the USAF in extensive thermal stability programmes.

The basic principles of the HLPS are shown in figure 4. As shown in figure 4, 1 litre of test fuel is pressurised in a stainless steel reservoir to 500psi. The fuel is then pumped *via* a pre-filter over a heated test section (@335°C). As deposition occurs on both the tube and in the fuel bulk the bulk deposit is measured as a filter drop change across a 17 micron filter. A pressure transducer cell measures the rate of pressure drop (in mmHg min-1). Finally the spent fuel is returned to the top of the reservoir, separated by an appropriate seal.

Apparatus - Alcor HLPS – is a modular version of the equipment set up as defined in ASTM D-3241. The test section must be of stainless steel 316 and free from grease. The filter to be used must be of 17 micron mesh as supplied by Alcor.

Materials

Base fuels – are fuels free of additives

Additized fuels - are base fuels containing 100 mg/l (active ingredient) of detergent/dispersant alone.

Main Test Procedure

Sample Preparation

1. Filter 1 litre of base test fuel through a 0.7 micron filter.
2. If fuel is to be additised transfer the known weight of additive(s) to a 1 litre volumetric flask using base test fuel.
3. Transfer the test fuel to a 2 litre beaker. Aerate using the glass bubbler attachment for a minimum of 6 minutes. Test run must be initiated within 1 hour of aeration.
4. Transfer the test fuel to the stainless steel reservoir.
5. Check the piston seal for degradation. If OK place the piston head on the surface of the fuel and push down using the supplied handle until fuel begins to seep up from the reservoir.
6. Place the large 'O' ring seal in the reservoir top and secure to the top of the reservoir using a socket wrench.
7. Connect the connector tube from the filter unit to the test cell using new 'O' ring.
8. Connect all remaining pipe-work using new 'O' rings.

Main Test Run Procedure.

1. Close BLEED valve on front of HLPS and open PRESSURISE valve. Ensure that system is pressurised to 500 psi.
2. Ensure that lower knob on delta P cell is turned to BYPASS and upper knob is VENT CLOSED.
3. Switch on PUMP. Red indicator light will come on. Ensure that FUEL FLOW CONTROL is set to 230. This equates to a flow rate of 3 mls/min.
4. Allow fuel to pump round system until a steady drop rate is seen through the perspex window on top of the fuel reservoir. When steady count the time taken for 20 drops. If the time is 9 secs. +/- 1 seconds this is acceptable for 3 mls/min.
5. Ensure that HEATER TUBE TEMP. CONTROL is set to 335 deg. C. Switch on HEATER. Red indicator light will come on. Needle will then rise to the vertical. Heater power is controlled by using the POWER CONTROL dial. A typical setting for this procedure is 82 +/- 10 volts.
6. Switch on the differential pressure module (DPM) by depressing the POWER button.
7. When needle reads correct temperature switch the delta P lower knob to RUN. This will divert the fuel flow through the differential pressure cell.
8. Allow the pressure read out on the differential pressure module to equilibrate and

press RECORD. The differential pressure will be recorded every 5 minutes on the in-built printer.

9. Allow the test to run whilst monitoring the differential pressure change. The DPM has an alarm setting that will cause multi-point printing at 125 mmHg. If the differential pressure rises above 300 mmHG turn the lower DPM knob to bypass and note the time.
10. In all cases allow the test run to complete a 5 hour test sequence. The HLPS will shut down automatically after 5 hours.

Analysis - Analysis is carried out on the Leco Carbon Analyser RC412.

Results - Are quoted for 2 readings.
Filter blockage - Record the change in differential pressure during the run. Results are quoted in mmHg min-1, e.g. 300/45, 0/300. The first figure is the change in differential pressure in mmHg the latter the time in minutes
Carbon deposit weight - Record the value according to method no. JP8003/01 in μgcm^{-2}.

PROTOCOL III - MSEP

The MSEP testing is carried out in a fuel dosed with

- 2 mg/l DINNSA Stadis 450 (static dissipater),
- 12 mg/l DCI 4A (corrosion inhibitor),
- 0.15vol%DIEGME (icing inhibitor),

The dosed fuel makes up a standard military basefuel package for purposes of MSEP evaluation. The detergent/dispersant has been added to this at treat rate of 50 mg/l (active ingredient). The tests are carried out using a modified MSEP cell supplied as MCELL by Emcee Electronics Inc. The MSEP test was otherwise performed in accordance with ASTM Designation D3948-93. Details of this D3948-93 are given in Appendix I.

SYNTHESES

PIBSIs

1000/ Butylamine PIBSI

1000 mwt Glissopal derived PIBSA (467.6g) was stirred with Shellsol AB (311.8g) in a 1l oil jacketed reactor equipped with an overhead stirrer, thermometer and Dean & Stark trap. Whilst still at room temperature butylamine (31.5g) was added in one aliquot with continued stirring. An immediate exotherm was noted. The reaction mix was heated to ~150°C for three hours whilst removing water. 720g of product was isolated.

Analysis of the product showed it to contain 40%m/m solvent, 0.81%m/m nitrogen.

1000/ AEEA PIBSI

1000 mwt Glissopal derived PIBSA (633.2g) was stirred with Shellsol AB (421g) in a 1l oil jacketed reactor equipped with an overhead stirrer, thermometer and Dean & Stark trap. Whilst still at room temperature aminoethylethanolamine (60.6g) was added in one aliquot with continued stirring. An immediate exotherm was noted. The reaction mix was heated to 130-150°C for three hours whilst removing water. 1058g of product was isolated.

Analysis of the product showed it to contain 39%m/m solvent, 1.47%m/m nitrogen.

1000/bis EDA PIBSI

1000 mwt Glissopal derived PIBSA (270.08) was stirred with Shellsol AB (180.1g) in a 1l oil jacketed reactor equipped with an overhead stirrer, thermometer and Dean & Stark trap. The solution was heated to 112°C and ethylene diamine (6.17g) was added over 20 minutes with continued stirring. An exotherm was noted. The reaction mix was heated to 150-160°C for three hours whilst removing water. 422g of product was isolated.

Analysis of the product showed it to contain 37%m/m solvent, 0.49%m/m nitrogen.

2300/ Butylamine PIBSI

1000 mwt Glissopal derived PIBSA (467.6g) was stirred with Shellsol AB (311.8g) in a 1l

oil jacketed reactor equipped with an overhead stirrer, thermometer and Dean & Stark trap. Whilst still at room temperature butylamine (31.5g) was added in one aliquot with continued stirring. An immediate exotherm was noted. The reaction mix was heated to ~150°C for three hours whilst removing water. 720g of product was isolated.

Analysis of the product showed it to contain 40%m/m solvent, 0.81%m/m nitrogen.

2300/ bis EDA

2300 mwt Glissopal derived PIBSA in Shellsol (302g, 21.6% solvent) was stirred with extra Shellsol AB (95g) in a 1l oil jacketed reactor equipped with an overhead stirrer, thermometer and Dean & Stark trap. Ethylenediamine (2.79g)was added at room temperature whilst stirring. The reaction mix was heated to 120°C for 2 hours and then 140°C for 2 hours whilst removing water. 501g of product was isolated.

1000/ ammonia

1000 mwt Glissopal derived PIBSA (450.15g) was stirred with Shellsol AB (298.99g) in a 1l oil jacketed reactor equipped with an overhead stirrer, thermometer, Dean & Stark trap and a dip tube through which to add ammonia. The temperature was taken up to 138°C and the ammonia gas (5.81g) was added over 3 hours, whilst collecting water in the trap. Heating was continued for a further 2 hours. 731g of product was isolated.

Analysis of the product showed it to contain 40 %m/m solvent, 0.76 %m/m nitrogen.

PIBamine

PIB chloride (153g, chlorine content 4.89% m/m) was placed in a stirred reactor with butylamine (61.6g) and Shellsol (50 ml. The reactor contents were heated to reflux for 19.5 hours. Crystalline solid could be seen in the solution as the reaction proceeded. The reaction was allowed to cool and an excess of aqueous sodium carbonate was mixed with the reactor contents. After separation the organics were washed with water and dried over sodium sulphate. The unreacted butylamine was removed under reduced pressure leaving the 190g product plus solvent.

Analysis of the product showed it to contain 23% m/m solvent, 0.95% m/m nitrogen, 1% m/m residual chlorine.

Mannich Compounds

The Mannichs for use in the present invention may be synthesised in accordance with the teaching of EP 0831141.

RESULTS

The following data were obtained. For the sake of clarity the compounds in accordance with the present invention are shown in bold.

Chemistry	Compound	No. of Nitrogens	FUEL				
			POSF 3684	Shell Hydrotreated	POSF 3684		Shell Hydrotreated
			ICOT % efficiency		HLPS ΔP/min	Carbon burnoff µg/cm^2	MSEP
	None – Control		-	-	300/45	125	74,79,80
PIBSIs	**1000/m/ButA**	**1**	**71.9**	**46.4**	-		**80**
	1000/m/EDA	2	51.3	58.8	-		0
	1000/b/EDA	**2**	**75.5**	**61.4**	-		**75**
	1000/m/AEEA	2	89.3	58.8	-		0
	1000/b/TEPA	5	96	87	-		0
	2300/m/TEPA	5	93.3	68.2	0/300	50.4	0
PIBamines	**1000/ButA**	**1**	**71.4**	**62.3**	**300/195**	**104**	**77,81**
	1000/EDA, DMAPA	2	49.6	60.1	-		70
Mannichs	**780/ButA**	**1**	**66.5**	**65.3**	**4/300**	**95.6**	**81**
	1000/ButA	**1**	**72.3**	**59.4**	**6/300**	**74**	**74,76**
	2300/ButA	**1**	**92.4**	**54.2**	**12/300**	**90.5**	**75**
	780/TEPA	5	6.2	44.5	-		0

The present data clearly show that the compounds for use in the composition of the present invention exhibit detergency and/or dispersancy in the thermal stability testing but does not cause MSEP to drop from "basefuel".

All publications mentioned in the above specification are herein incorporated by reference. Various modifications and variations of the described methods and system of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed

should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims

CLAIMS

1. A composition comprising

(i) an aviation fuel; and

(ii) a deposit inhibiting compound of the formula I

P-Q-R (I)

in which P is a polymeric hydrocarbyl group

in which Q is an optional ring system;

in which R is a group selected from H and hydrocarbyl;

wherein if R is a hydrocarbyl group it is free of a carboxylic acid group (-COOH);

wherein Q together with R contains no greater than 2 nitrogens; and

wherein when Q together with R contains 2 nitrogens each of the nitrogens is a member of a heterocyclic ring.

2. A composition according to claim 1 wherein Q together with R contains no greater than 1 nitrogen.

3. A composition according to claim 1 or 2 wherein Q together with R contains no greater than 1 basic nitrogen.

4. A composition according to any one of the preceding claims wherein if R is a hydrocarbyl group it is free of a hydroxyl group (-OH).

5. A composition according to any one of the preceding claims wherein the optional ring system Q is present.

6. A composition according to any one of the preceding claims wherein Q is substituted.

7. A composition according to any one of the preceding claims wherein Q is substituted with one or more groups selected from =O and -OH

8. A composition according to any one of the preceding claims wherein Q is an aromatic ring.

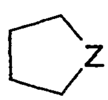
9. A composition according to any one of the preceding claims wherein Q has from 4 to 10 members.

10. A composition according to any one of the preceding claims wherein Q has from 4 to 6 members.

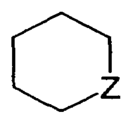
11. A composition according to any one of the preceding claims wherein Q has 5 or 6 members.

12. A composition according to any one of the preceding claims wherein Q is a carbon ring or a heterocyclic ring containing carbon and one nitrogen.

13. A composition according to any one of the preceding claims wherein Q is selected from a ring system of the formula

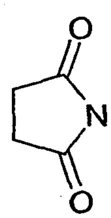


or



wherein Z is C or N.

14. A composition according to any one of the preceding claims wherein Q is selected from a ring system of the formula



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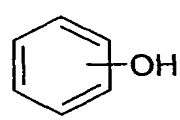


15. A composition according to any one of the preceding claims wherein P is a hydrocarbyl group having from 10 to 200 carbons.

16. A composition according to any one of the preceding claims wherein P is a branched or straight chain alkyl group.

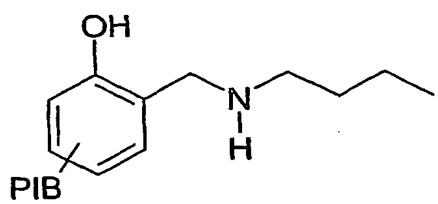
17. A composition according to any one of the preceding claims wherein P is a branched alkyl group.

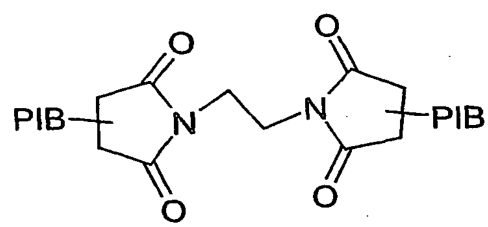
18. A composition according to any one of the preceding claims wherein P is polyisobutene.

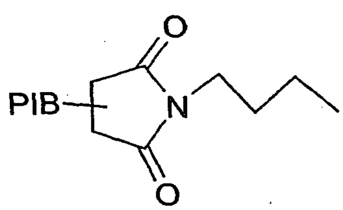
19. A composition according to any one of the preceding claims wherein P has a molecular weight of from 700 to 2300.

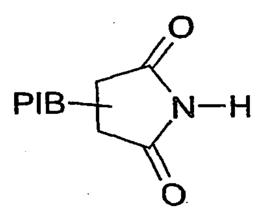
20. A composition according to any one of the preceding claims wherein P is polyisobutene having a molecular weight of from 800 to 1200.

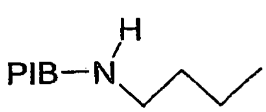
21. A composition according to any one of the preceding claims wherein the deposit inhibiting compound is selected from compounds of the formulae











wherein PIB is polyisobutene.

22. A composition according to claim 21 wherein PIB is polyisobutene having a molecular weight of from 800 to 1000.

23. A composition according to any one of the preceding claims wherein the aviation is a jet fuel.

24. A composition according to any one of the preceding claims wherein the fuel is JP-8 aviation fuel.

25. A method for inhibiting deposition formation in a fuel at a temperature of from 100 to 335°C, the method comprising combining with the fuel a deposit inhibiting compound of the formula I

P-Q-R (I)

in which P is a polymeric hydrocarbyl group; in which Q is an optional ring system; in which R is a group selected from H and hydrocarbyl; wherein if R is a hydrocarbyl group it is free of a carboxylic acid group (-COOH); wherein Q together with R contains no greater than 2 nitrogens; and wherein when Q together with R contains 2 nitrogens each of the nitrogens is a member of a heterocyclic ring.

26. A method according to claim 25 wherein the deposit inhibiting compound is a defined in any one of claims 2 to 22.

27. A method according to claim 25 or 26 wherein the fuel is an aviation fuel.

28. Use of a deposit inhibiting compound as defined in any one of claims 1 to 22 for

(i) the inhibition of deposit formation in a composition comprising the compound and a fuel; and/or

(ii) the inhibition of particle formation from the oxidation product(s) of a fuel; and/or

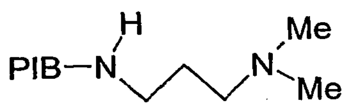
(iii) the solubilisation of deposits and/or deposit precursors

29. A use according to claim 28 wherein the fuel is an aviation fuel.

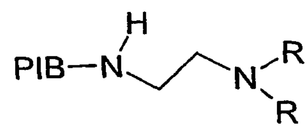
30. A fuel composition as substantially herein before described with reference to any one of the Examples.

31. A use as substantially herein before described with reference to any one of the Examples.

32. A use as substantially herein before described with reference to any one of the Examples.

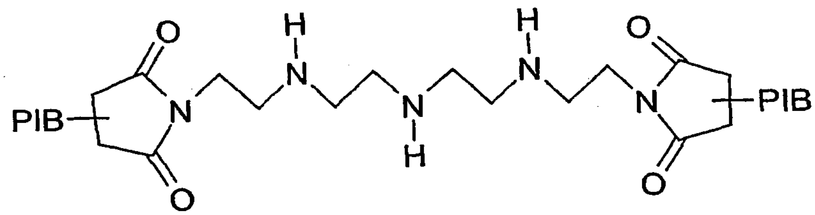


PIBamines

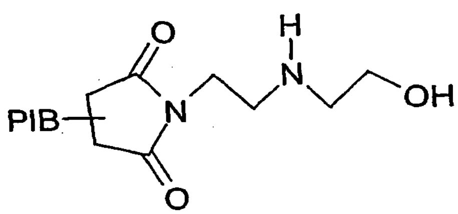


(R=H or Me)

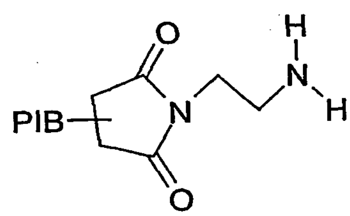
1000/EDA,DMAPA



1000/b/TEPA PIBSI

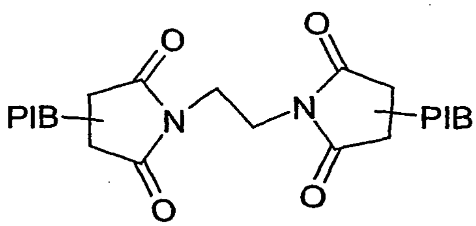


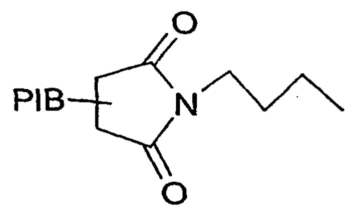
1000/m/AEEA PIBSI

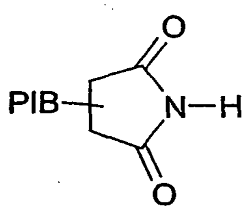


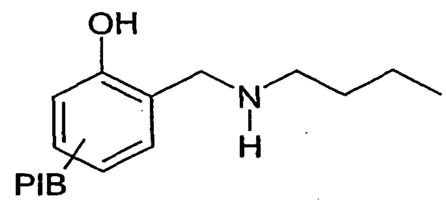
1000/m/EDA PIBSI

Figure 1


1000/b/EDA PIBSI


1000/m/ButA PIBSI


Ammonia PIBSI (butylamine)


ButA Mannich

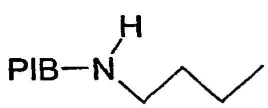

1000/ButA

Figure 2

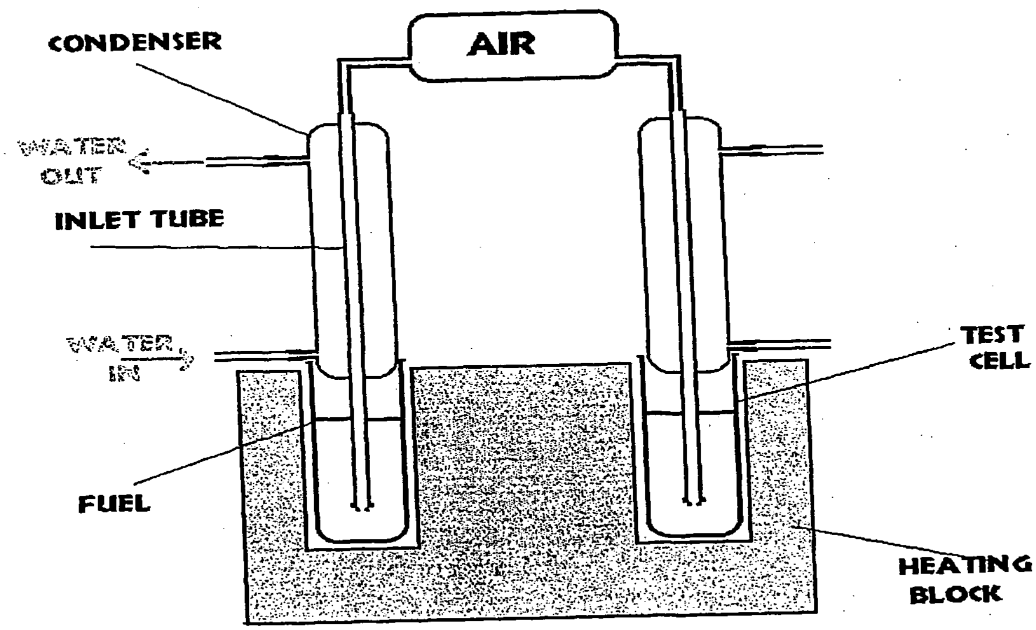

CONDENSER
AIR
WATER OUT
INLET TUBE
WATER IN
TEST CELL
FUEL
HEATING BLOCK

Figure 3

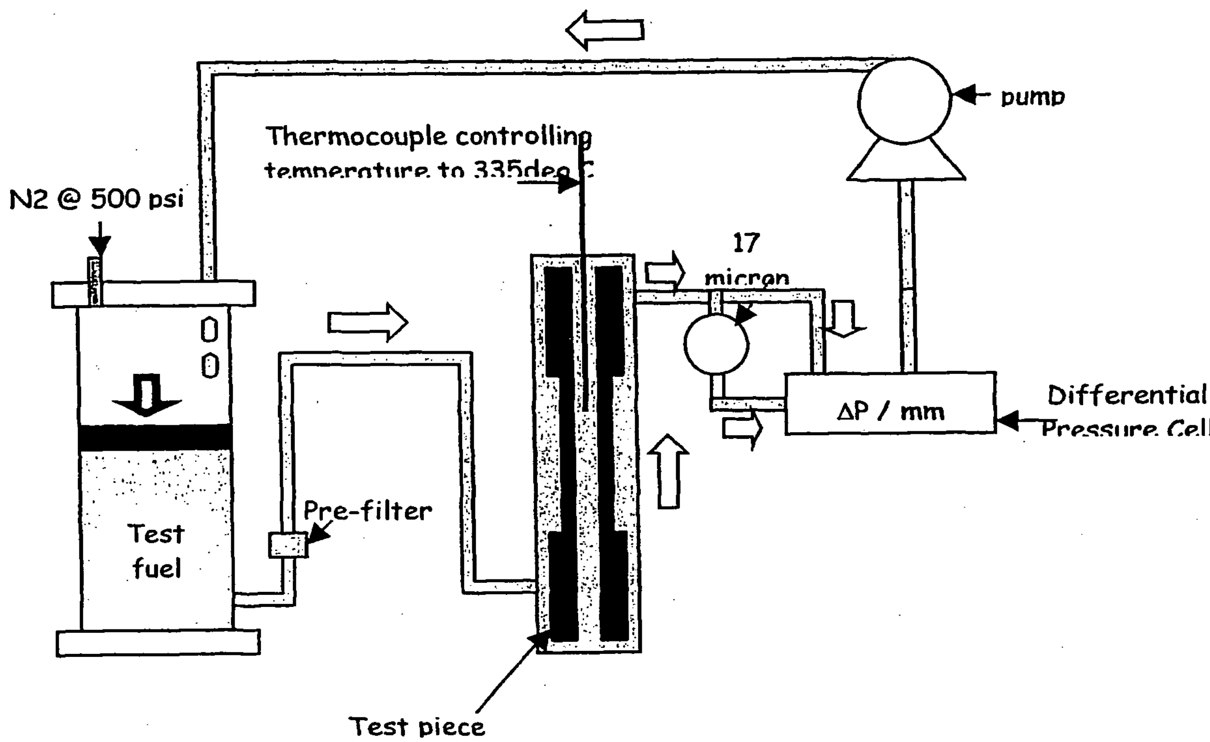

pump
Thermocouple controlling temperature to 335deg C
N2 @ 500 psi
17 micron
Differential Pressure Cell
ΔP / mm
Test fuel
Pre-filter
Test piece

Figure 4

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

PCT

(43) International Publication Date
3 October 2002 (03.10.2002)

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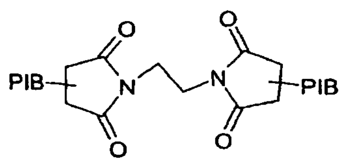
[Continued on next page]

(54) Title: COMPOSITION



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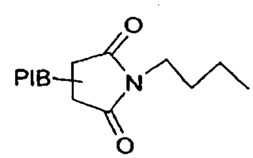
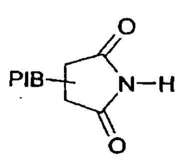
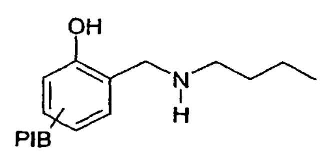


1000/m/ButA PIBSI



Ammonia PIBSI (butylamine)



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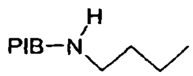

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(57) Abstract: The present invention provides a composition comprising (i) an aviation fuel; and (ii) a deposit inhibiting compound of the formula P-Q-R in which P is a polymeric hydrocarbyl group in which Q is an optional ring system ; in which R is a group selected from H and hydrocarbyl; wherein if R is a hydrocarbyl group it is free of a carboxylic acid group (-COOH); wherein Q together with R contains no greater than 2 nitrogens; and wherein when Q together with R contains 2 nitrogens each of the nitrogens is a member of a heterocyclic ring.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10L1/22 C10L10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	EP 0 182 940 A (MOBIL OIL CORP) 4 June 1986 (1986-06-04) page 7, paragraph 4; claims 1-8,10-20,24 ---	1-12, 14-18, 23,25-29
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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International Application No
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